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PATENT SPECIFICATION

NO DRAWINGS

1,136,539

1,136,539

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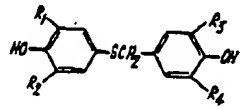
COMPLETE SPECIFICATION

Phenolic Sulphides

We, UNIROYAL, INC., a corporation of the State of New Jersey, one of the United States of America, of 1230, Avenue of the Americas, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing 3,5-dialkyl-4-hydroxybenzyl 3,5-dialkyl-4-hydroxyphenyl sulphides.

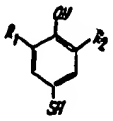
These compounds are represented by the following formula:



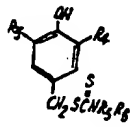
wherein R_1, R_2, R_3 and R_4 are alkyl groups of 1 to 8 carbon atoms each.

The compounds produced by this process are useful as antioxidants and have been previously described, and generically disclosed in U.S. patent 3,179,701. The present invention provides a method of preparing 3,5-dialkyl - 4 - hydroxybenzyl 3,5 - dialkyl - 4 - hydroxyphenyl sulfides from readily available and inexpensive intermediates which can be readily prepared in high yield and high purity.

The present invention comprises a method of preparing 3,4-dialkyl-4-hydroxybenzyl 3,5-dialkyl-4-hydroxyphenyl sulfides by reacting a mercaptophenol of the general formula:

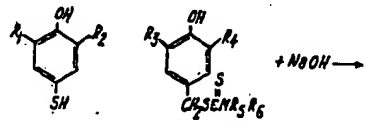


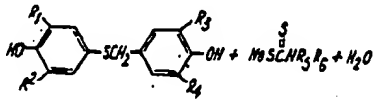
wherein R_1 and R_2 are alkyl groups of 1 to 8 carbon atoms each, with a compound of the general formula:



wherein R_3 and R_4 are alkyl groups of 1 to 8 carbon atoms each and R_5 and R_6 are lower alkyl groups, with an alkali metal hydroxide, e.g. sodium hydroxide. It is preferred to use equimolar amounts of the mercaptophenol, dithiocarbamate and alkali metal hydroxide.

The equation for this reaction is:





[Price 4s. 6d.]

The reaction is conveniently carried out in an aqueous reaction medium. The reaction medium preferably contains a water-miscible solvent such as lower alkanol or an ether such as methanol, ethanol, isopropanol, dioxane or ethylene glycol dimethyl ether. The reaction is preferably effected at a temperature from room temperature to 100°C.

Preferred solvents for the reaction are methanol, ethanol and isopropanol. The preferred temperature is in the range of 50°C. to 100°C., the reaction ordinarily being carried out at or near the reflux temperature of the solution. The preferred time of the reaction is up to four hours. Longer times may be used but are not necessary, the reaction generally being complete in 30 minutes or less.

The reaction may also be carried out in a two-phase system such as benzene-water or xylene-water, using vigorous agitation. Although longer reaction times are generally employed than in homogeneous solutions, this heterogeneous system has the advantage of providing a simplified recovery procedure. In such a two-phase system, the product is soluble in the organic phase which can be readily separated from the aqueous phase containing the alkali metal dialkyldithiocarbamate. The product is then obtained by removing the solvent from the organic phase.

Any alkali metal hydroxide may be used with sodium hydroxide being preferred.

The mercaptophenols which may be used include: 2,6 - dimethyl - 4 - mercaptophenol; 2,6 - diisopropyl - 4 - mercaptophenol; 2 - methyl - 4 - mercapto - 6 - t - butylphenol; 2,6 di - sec - butyl - 4 - mercaptophenol; 2,6 di - t - butyl - 4 - mercaptophenol; 2 - methyl - 4 - mercapto - 6 - octylphenol; and 2,6 - di - t - octyl - 4 - mercaptophenol.

The intermediate 3,5 - dialkyl - 4 - hydroxybenzyl N,N - dialkyldithiocarbamates may be prepared by the reaction of a 2,6-dialkylphenol with formaldehyde, a dialkylamine and carbon disulfide in a manner as described by in U.S. patents 2,757,174 and 3,117,947. The phenols which may be used include: 2,6 - dimethylphenol; 2 - methyl - 6 - t - butylphenol; 2,6 - diisopropylphenol; 2,6 - di - t - butylphenol; 2,6 - di - sec - butylphenol; 2 - methyl - 6 - octylphenol, and 2,6 - dioctylphenol. Any convenient dialkylamine may be used but the low molecular weight members in which the alkyl groups contain one to five carbon atoms are preferred.

To illustrate the invention method the following examples are given In the examples, the proportions are expressed in parts by weight unless otherwise noted and all temperatures are recorded in centigrade.

EXAMPLE 1

The preparation of 3,5-di-t-butyl-4-hydroxybenzyl 3,5 - di - t - butyl - 4 - hydroxyphenyl sulfide.

To a solution of 14.3 g. (0.06 mole) of 2,6 - di - t - butyl - 4 - mercaptophenol and 4.8 g. (0.06 mole) of 50% aqueous sodium hydroxide in 100 ml. of ethanol was added 20.4 g. (0.06 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyl-dithiocarbamate. The reaction mixture was refluxed gently for a few minutes and the solution was then poured into water. The product which separated was extracted with ether. The ether solution was washed with water, dried with anhydrous sodium sulfate and evaporated down to a residue which was triturated with hexane to give a crystalline product. The product was filtered off and washed with cold hexane to yield 23.5 g. (86%) of 3,5-di - t - butyl - 4 - hydroxybenzyl 3,5 - di - t - butyl - 4 - hydroxyphenyl sulfide, m.p. 119—121°. Recrystallization raised the melting point slightly to 122—123°.

EXAMPLE 2

The preparation of 3,5 - di - t - butyl - 4 - hydroxybenzyl 3 - methyl - 4 - hydroxy - 5 - t - butylphenyl sulfide.

To a solution of 19.6 g. (0.1 mole) of 2-methyl - 4 - mercapto - 6 - t - butylphenol and 8.8 g. (0.11 mole) of 50% aqueous sodium hydroxide in 100 ml. of ethanol was added 33.9 g. (0.1 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The reaction mixture was refluxed gently for ten minutes. It was then diluted slowly with 100 ml. of water in small portions and cooled. The white crystalline precipitate which formed was filtered off, washed with aqueous ethanol and dried yielding 34.1 g. (82.5%) of 3,5-di-t-butyl-4-hydroxybenzyl 3 - methyl - 4 - hydroxy - 5 - t - butyl - phenyl sulfide, m.p. 91—95°. Recrystallization from hexane raised the melting point to 95—96°.

EXAMPLE 3

The preparation of 3-methyl-4-hydroxy-5-t - butylbenzyl 3 - methyl - 4 - hydroxy - 5-t-butylphenyl sulfide.

To a solution of 19.6 g. (0.1 mole) of 2-methyl - 4 - mercapto - 6 - t - butylphenol and 29.7 g. (0.1 mole) of 3-methyl-4-hydroxy-5-t-butylphenzyl N,N-dimethyldithiocarbamate in 100 ml. of benzene in a 500 ml. 3-neck Morton flask was added 8.4 g. (0.105 mole) of 50% aqueous sodium hydroxide in 100 ml. of water. The mixture was stirred vigorously for 2-1/2 hours at 70°C. and then cooled. The benzene layer was separated, washed with water, dried over anhydrous sodium sulfate and evaporated down to a viscous liquid residue. The last traces of solvent were removed *in vacuo* to yield 37 g. (99.5%) of 3-methyl-4-hydroxy-5-t-butylbenzyl 3-methyl-4-hydroxy-5-t-butylphenyl sulfide as a viscous oil. The structure of the product was confirmed by its infrared spectrum.

EXAMPLE 4

The preparation of 3,5-dimethyl-4-hydroxybenzyl 3-methyl-4-hydroxy-5-t-butylphenyl sulfide.

To a solution of 19.6 g. (0.1 mole) of 2-methyl-4-mercapto-6-t-butylphenol and 8 g. (0.1 mole) of 50% aqueous sodium hydroxide in 100 ml. of ethanol was added 25.5 g. (0.1 mole) of 3,5-dimethyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The reaction mixture was refluxed gently for 15 minutes. It was then cooled and poured into cold water. The product which separated was extracted with ether. The ether extract was evaporated to give 3,5-dimethyl-4-hydroxybenzyl 3 - methyl - 4 - hydroxy - 5 - t - butylphenyl sulfide as a viscous oil.

EXAMPLE 5

The preparation of 3,5-diisopropyl-4-hydroxybenzyl 3 - methyl - 4 - hydroxy - 5 - 2-butylphenyl sulfide.

To a solution of 19.6 g. (0.1 mole) of 2-methyl - 4 - mercapto - 6 - t - butylphenol and 8 g. (0.1 mole) of 50% aqueous sodium hydroxide in 150 ml. of ethanol was added 31.1 g. (0.1 mole) of 3,5-diisopropyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The mixture was refluxed gently for 20 minutes. It was then poured into water and the product which separated was extracted with ether. The ether extract was washed with water, dried with anhydrous sodium sulfate and evaporated to give a quantitative yield of 3,5-diisopropyl-4-hydroxybenzyl 3-methyl-4-hydroxy-5-t-butylphenyl sulfide as a viscous oil.

EXAMPLE 6

The preparation of 3,5-di-t-butyl-4-hydroxybenzyl 3,5-diisopropyl-4-hydroxyphenyl sulfide.

To a solution of 10.5 g. (0.05 mole) of 2,6-diisopropyl-4-mercaptophenol and 4 g. (0.05 mole) of 50% aqueous sodium hydroxide in 150 ml. of ethanol was added 17 g. (0.05 mole) of 3,5-di-t-butyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The mixture was refluxed for 20 minutes. It was then cooled and poured into cold water. The product which separated was extracted with ether and the extract was evaporated to yield 3,5 - di - t - butyl - 4 - hydroxybenzyl 3,5 - diisopropyl-4-hydroxyphenyl sulfide as a viscous oil.

EXAMPLE 7

The preparation of 3,5 - di - t - butyl - 4-hydroxybenzyl 3,5-dimethyl-4-hydroxyphenyl sulfide.

To a solution of 15.4 g. (0.1 mole) of 2,6-dimethyl-4-mercaptophenol and 8 g. of 50% aqueous sodium hydroxide in 150 ml. of ethanol was added 34 g. (0.1 mole) of 3,5-di - t - butyl - 4 - hydroxybenzyl N,N-dimethyldithiocarbamate. The mixture was refluxed for 25 minutes. It was then cooled and poured into water. The product which separated was extracted with ether. The ether extract was washed with water, dried with anhydrous sodium sulfate and evaporated to a residue which slowly crystallized. It was broken up and washed twice with hexane giving 25.2 g. (69% yield) of 3,5-di-t-butyl - 4 - hydroxybenzyl 3,5 - dimethyl - 4 - hydroxyphenyl sulfide, m.p. 65—67°. The melting point was raised to 67—68° on recrystallization from hexane.

EXAMPLE 8

The preparation of 3-methyl-4-hydroxy-5-t-butylbenzyl 3,5 - di - t - butyl - 4 - hydroxyphenyl sulfide.

To a solution of 5.7 g. (0.024 mole) of 2,6-di - t - butyl - 4 - mercaptophenol and 2 g. (0.025 mole) of 50% aqueous sodium hydroxide in 25 ml. of ethanol was added 7.1 g. (0.024 mole) of 3-methyl-4-hydroxy-5-t-butylbenzyl N,N-dimethyldithiocarbamate. The mixture was refluxed for 10 minutes. It was then poured into water and the product which separated was extracted with hexane. The hexane solution was cooled and the 3-methyl - 4 - hydroxy - 5 - t - butylbenzyl 3,5-di-t-butyl-4-hydroxyphenyl sulfide crystallized out, m.p. 102—103°.

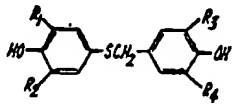
EXAMPLE 9

The preparation of 3,5-dimethyl-4-hydroxybenzyl 3,5-di-t-butyl-4-hydroxyphenyl sulfide.

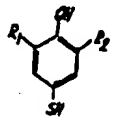
To a solution of 19 g. (0.08 mole) of 2,6-di - t - butyl - 4 - mercaptophenol and 6.4 g. (0.08 mole) of 50% aqueous sodium hydroxide in 100 ml. of ethanol was added 20.4 g. (0.08 mole) of 3,5-dimethyl-4-hydroxybenzyl N,N-dimethyldithiocarbamate. The mixture was refluxed for 15 minutes. It was then poured into water and the product which separated was extracted with ether. The ether extract was evaporated leaving 3,5-dimethyl - 4 - hydroxybenzyl 3,5 - di - t - butyl-4-hydroxyphenyl sulfide as a viscous oil.

WHAT WE CLAIM IS:—

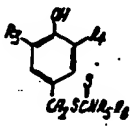
1. A process for preparing a compound of the formula:



in which R_1, R_2, R_3 and R_4 are alkyl groups of 1 to 8 carbon atoms each, which comprises reacting a mercaptophenol of the general formula:



wherein R_1 and R_3 are alkyl groups of 1 to 8 carbon atoms, with a compound of the general formula:



wherein R_2 and R_4 are alkyl groups of 1 to 8 carbon atoms and R_5 and R_6 are lower alkyl groups, and an alkali metal hydroxide.

2. A process as claimed in claim 1 wherein the reaction is effected in an aqueous reaction medium.

3. A process as claimed in claim 1 or claim 2 wherein the reaction medium contains a water-miscible organic solvent.

4. A process as claimed in claim 3 wherein the organic solvent is a lower alkanol or an ether.

5. A process as claimed in claim 4 wherein the organic solvent is methanol, ethanol, isopropanol, dioxane or ethylene glycol dimethyl ether.

6. A process as claimed in claim 1 or claim 2 wherein the reaction is effected in a two-phase system.

7. A process as claimed in claim 6 wherein the two phase system is benzene-water or xylene-water.

8. A process as claimed in any one of the preceding claims wherein the alkali metal hydroxide is sodium hydroxide.

9. A process as claimed in any one of the preceding claims wherein equimolar amounts of mercaptophenol, dithiocarbamate and alkali metal hydroxide are employed.

10. A process as claimed in any one of the preceding claims wherein the reaction is effected at a temperature of from ambient temperature to 100°C.

11. A process as claimed in claim 10 wherein the reaction is effected at a temperature of from 50° to 100°C.

12. A process as claimed in any one of the preceding claims wherein R_5 and R_6 contain from 1 to 5 carbon atoms each.

13. A process as claimed in any one of the preceding claims wherein at least one of R_1, R_2, R_3 and R_4 represents a t-butyl group.

14. A process as claimed in claim 13 wherein R_1, R_2, R_3 and R_4 all represent t-butyl groups.

15. A process as claimed in claim 1 substantially as herein described.

16. A process as claimed in claim 1 substantially as herein described with references to the foregoing Examples.

17. 3,5 - Dialkyl - 4 - hydroxybenzyl 3,5 - dialkyl-4-hydroxyphenyl sulphides whenever prepared by a process as claimed in any one of the preceding claims.

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